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FORMATION OF γ-Al_2O_3 IN REACTION COATINGS PRODUCED WITH LASERS

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Introduction

Plating aluminum base alloys with a ceramic coating may improve their surface properties (hardness, wear resistance) keeping the advantages of aluminum as a light weight bulk material unchanged. In general laser cladding is a versatile technique to coat a substrate without affecting its bulk properties too much. However, cladding aluminum base systems with a ceramic coating is rather complicated [1,2]. Firstly, the melting points of several ceramic materials are close to the boiling temperature of Al and, secondly, the wet-ability between liquid aluminum and most ceramics is bad while rapid solidification during laser processing requires good wetting between the liquid metal and the solid ceramic within a very short time elapse.

The above-mentioned drawbacks may be tackled by promoting an exothermic chemical reaction at the interface between the metallic substrate and the ceramic coating [2]. The heat generated by this reaction lowers the laser energy density needed to melt the ceramic material. Another advantage is that the heat generated by this reaction is produced only locally.

In this work an Al base material is coated with an Al_2O_3 layer by cladding a mixture of Cr_2O_3 and Al powders (powder molar powder ratio Cr_2O_3: Al = 1:6). The heat generated by the laser beam radiation initiates an exothermic reaction between Cr_2O_3 and Al, to form an Al_2O_3 layer, according to:

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr.$$

Assuming a temperature of the melt pool of 1173 K, the exothermic heat generated by this reaction is 538 kJ/mole [3], which is used to heat the oxide layer.

In the past areas of γ-Al_2O_3 phase (cubic, a = 7.9 Å), next to the stable α-Al_2O_3 (rhombohedral, a = 4.759, c = 12.991) were found as a reaction product in the coating [2]. γ-Al_2O_3 is a transitional phase that usually forms by rapid cooling below 1200 K [3]. Because of rapid cooling the atoms cannot order to form stable α-Al_2O_3 and consequently the disordered γ-phase is formed. Above about 1200 K α-Al_2O_3 is formed [4]. The minimal temperature for γ-Al_2O_3 formation is around 800 K, found by experiments involving heating certain hydrates [5]. Cao et al [5] reported that laser-melted α-Al_2O_3 resolidifies as γ-Al_2O_3 due to the rapid cooling after pulsed laser irradiation. The benefit of the presence of γ-Al_2O_3 is the interface structure. The distorted structure allows more charged defects that may stabilize the interface and therefore decrease the interface energy and increase the interface strength. In

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addition, the smaller lattice misfits between γ-Al_2O_3/Al with respect to α-Al_2O_3/Al introduce less interface energy [6] [7].

This paper concentrates on the influence of the cooling rate on the amount of γ-Al_2O_3 that is formed in the coating during the laser process. In particular changing the laser processing parameters varies the cooling rate. The presence of γ-Al_2O_3 relative to α-Al_2O_3 was examined with X-ray diffraction (XRD).

Experimental

Laser cladding experiments were carried out with a 2kW Rofin Sinar Nd:YAG laser. The laser beam is transported by means of a fiber optic, resulting in a homogeneous intensity distribution (top hat). To avoid harmful reflections from the specimen back into the optical fiber, the laser beam is positioned under an angle 11° with respect to the substrate surface normal. Ar is used as a shielding gas to protect the lens as well as to reduce oxidation of the specimen. The specimen movement is realized by a CNC (computer numerical controlled) X-Y table. The specimen can be cooled to 15 °C as well as heated up to 300°C during the laser process.

In the experiments a commercial aluminum alloy (with 0.7 wt-% Mg, 0.4 wt-% Si) is used as substrate materials. Before laser treatment the surface is sand blasted to increase the absorptivity of laser light. A mixture of Cr_2O_3 and Al powder with molar ratio 1:6 is used as cladding material. The size distribution of Cr_2O_3 powder ranges between 20 and 40 μm, and that of aluminum between 60 and 100 μm. With a spot size of 2.4 mm, a laser power of 600 W was sufficient to initiate the reaction in the Cr_2O_3 + Al mixed powder.

During the cladding experiments the temperature is measured using a monochromatic Sensys 1994 fiber optical pyrometer, which detects the infrared radiation emitted from a body at a wavelength of 1.7 μm. The lens system, with a focal length of 27 cm, collects radiation from a spot size of 1.5 mm. The output data were obtained every 4 ms, during a period of 7.8 s. To minimize the contribution of the radiation of the laser (wavelength = 1.06 μm) the optical lens unit was protected with a sleeve of 23 cm, having an aperture of 5 mm. The optical lens unit of the pyrometer is oriented to the center of the laser track, fixed 15 mm from the beginning of the track, making an angle of 35° with the surface normal, sideward from the track. The distance between the track and aperture of the sleeve is 4 cm. By measuring the known substrate temperatures when the laser is switched off the pyrometer is roughly calibrated.

The crystallographic phases in the coatings were determined with X-ray diffraction (Philips PW-1830) using Cu-Kα radiation. The microstructure is analyzed with a Philips XL-30 FEG Scanning Electron Microscope (SEM) and a JEOL-4000EX/II high resolution Transmission Electron Microscope (TEM).

Results and Discussion

In order to study the dependence of γ-Al_2O_3 formation on the cooling rate, the cooling rate has to be varied. In the laser process two suitable experimental parameters, i.e. the scanning speed and substrate temperature are available to do this. The scanning speed, i.e. the speed of the table with respect to the laser beam, determines the interaction time that the surface of the track is exposed to the laser beam. The substrate temperature influences the absolute temperature change during the cooling process. In our experiments we used three substrate temperature conditions. The substrate is *cooled* and kept at 15°C or *heated* and kept at 300°C during the laser process. The third temperature condition is an *uncontrolled* substrate, i.e. the substrate starts at room temperature and is left free to change in temperature during the cladding process.

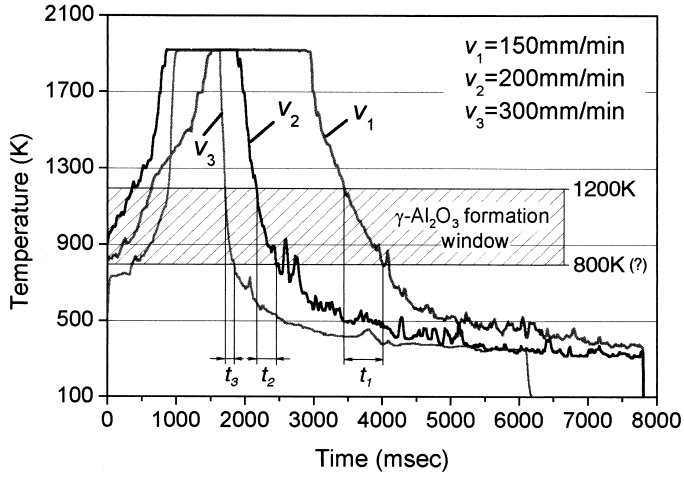

Figure 1. Temperature profiles, obtained with pyrometry, for laser cladding experiments with a laser power of P = 600 W and an *uncontrolled* substrate temperature. The scanning speed is varied.

Three temperature profiles of laser treatments on uncontrolled substrates with different scanning speeds (150, 200 and 300 mm/min) are shown in Fig. 1. At $t = 0$, the laser beam is approaching the area where the pyrometer is pointed to. When the laser beam enters this area the sample is heated up quickly to a temperature above the maximum temperature that can be detected by the pyrometer. The temperature decreases rapidly after the laser beam leaves the area. When the temperature gets below the limit of the pyrometer the temperature profile can be monitored again. In this work the cooling rate is calculated by slope of the curve when the temperature drops down from the maximum to about 250 K below this temperature. The temperature interval in which γ-Al_2O_3 forms is depicted in Fig. 1 by the hatched area.

The influence of the scanning speed, ranging from 50 mm/min to 700 mm/min, on the cooling is shown in Fig 2. All laser treatments, involved in this figure, were performed on an uncontrolled substrate. The cooling rate increased with increasing scanning speed. When the scanning speed is increased from 50 mm/min to 700 mm/min the cooling rate changes from 2100 K/s to 16000 K/s, respectively.

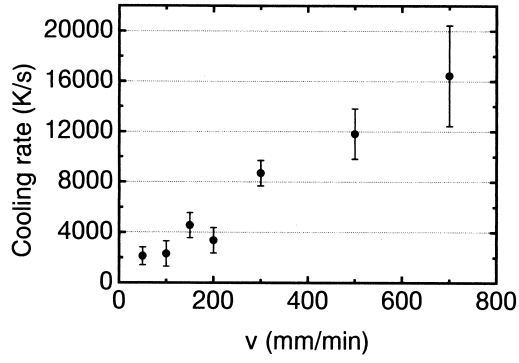

Figure 2. The cooling rate as a function of scanning speed for laser cladding experiments on an *uncontrolled* substrate.

TABLE 1
Cooling Rate of Laser Tracks Produced with Different Scanning Speeds and Substrate Temperature Conditions

v (mm/min)	Cooling rate (K/s)		
	Cooled (15°C)	Uncontrolled	Heated (300°C)
50	$(2.5 \pm 0.5) \cdot 10^3$	$(2.1 \pm 0.5) \cdot 10^3$	$(0.4 \pm 0.1) \cdot 10^3$
100	$(4 \pm 1) \cdot 10^3$	$(2.3 \pm 0.5) \cdot 10^3$	$(1.9 \pm 0.5) \cdot 10^3$
150	$(5 \pm 1) \cdot 10^3$	$(5 \pm 1.0) \cdot 10^3$	$(2.7 \pm 0.5) \cdot 10^3$

The cooling rates of experiments for the lower scanning speeds (50, 100 and 150 mm/min), performed with different substrate temperature conditions, are listed in Table 1 and visualized in Fig. 3. Heating the substrate decreases the cooling rate while cooling the substrate increases the cooling rate with respect to an uncontrolled substrate.

The scanning speed and substrate temperature conditions showed the expected influences on the cooling rate. Increasing the scanning speed results in a higher cooling rate because the surface is heated for a shorter time. Cooling the substrate to 15°C increases the temperature difference between coating and substrate and therefore the cooling rate is increased. Reversibly, the cooling rate is decreased when the substrate is heated to 300°C, because the temperature difference is less.

It is impossible, using XRD, to give exact quantitative values on the γ-Al_2O_3 content in the coating. However comparing the γ to α peak intensities may reveal three different categories: No γ-Al_2O_3, a low amount of γ-Al_2O_3 and a high amount of γ-Al_2O_3. It is important to take into account all the peaks of one phase, because strong textures are usually present in the laser coatings, caused by the enforced solidification direction due to the presence of temperature gradients. Texture affects the relative peak intensities, which may lead to erroneous conclusions when only the main peaks are included. Four XRD 2θ plots, with assigned α-Al_2O_3 and γ-Al_2O_3 peaks, are shown in Fig. 4. It is obvious that the measurements on the tracks clad at the lowest cooling rates (tracks produced with $v = 50$ mm/min, heated and uncontrolled substrate: Fig. 4a and c) show a high γ-Al_2O_3 content. Fig. 4d, v = 50 mm/min, cooled substrate, shows a medium amount of γ-Al_2O_3. The track with the highest cooling rate (Fig. 4b, track produced with $v = 700$ mm/min, uncontrolled substrate) almost no γ-Al_2O_3 peaks are detected. The same holds for XRD measurements performed on the other laser tracks obtained with different scanning speeds and substrate conditions: the higher the cooling rate the less γ-Al_2O_3 compared to α-Al_2O_3 is found. At the first sight this result looks in contradiction with the supposition that higher cooling rates promote the formation of the unstable γ-Al_2O_3. The fact that strong γ-Al_2O_3 peaks (Fig. 4c) are present in the coating produced with lowest cooling rate, 400K/s, demonstrates that this cooling

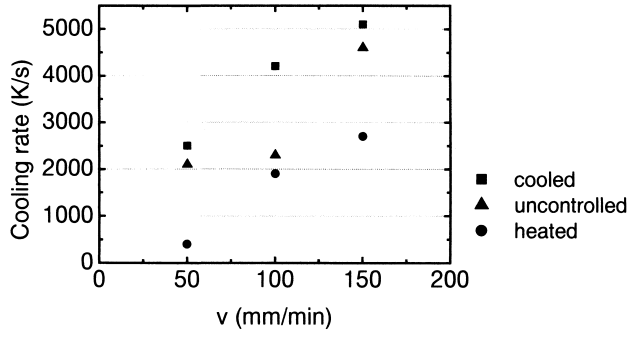

Figure 3. The cooling rate as a function of scanning speed for the three different substrate temperature conditions.

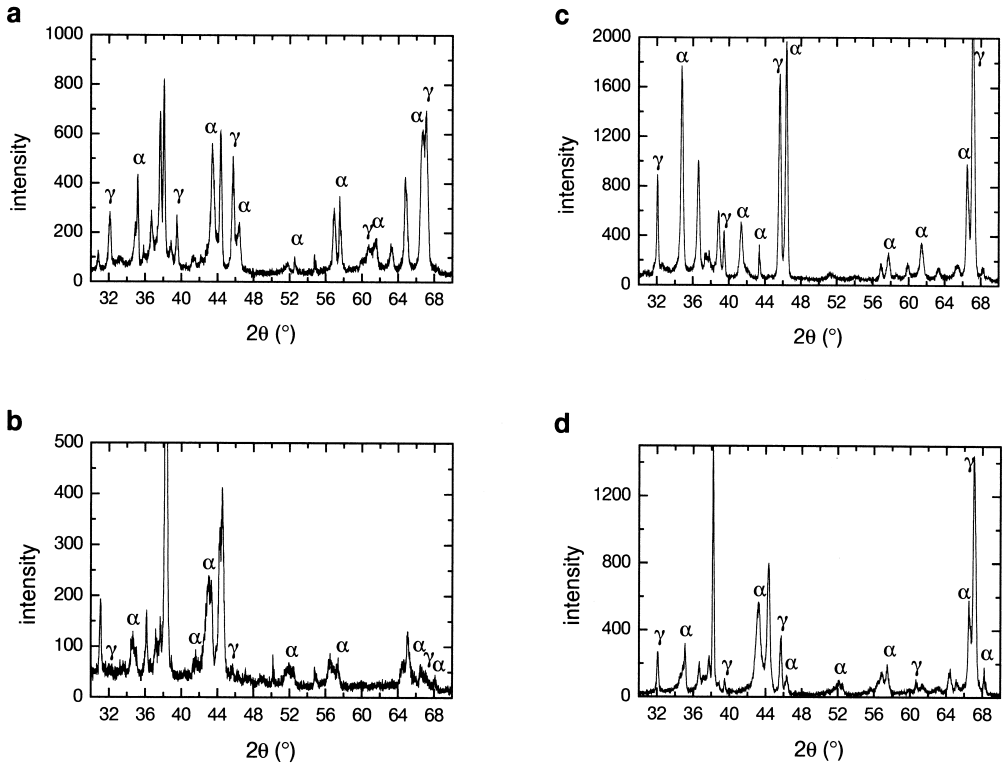

Figure 4. XRD spectra, with labeled α-Al_2O_3 and γ-Al_2O_3 peaks, on laser tracks produced with (a) v = 50 mm/min, substrate uncontrolled, (b) v = 700 mm/min, substrate uncontrolled, (c) v = 50 mm/min, substrate heated to 300°C and (d) v = 50 mm/min, substrate cooled to 15°C.

rate is high enough to freeze the unstable γ-Al_2O_3. The observation that with increasing cooling rate less γ-Al_2O_3 is found can be understood on the basis of Fig. 1. Looking at the temperature window in which γ-Al_2O_3 is formed (1200 K-800 K), the cooling rate determines the time that the coating is actually in this window. For the temperature profiles of Fig. 1 the cooling rate increases when the scanning speed is increasing, therefore the time to form γ-Al_2O_3 is shorter ($t_3 < t_2 < t_1$), and less γ-Al_2O_3 will be formed.

In general we may describe the process as follows: Due to the laser power intensity (133 W/mm^2) and heat formation during the reaction between Cr_2O_3 and Al, the temperature reaches values higher

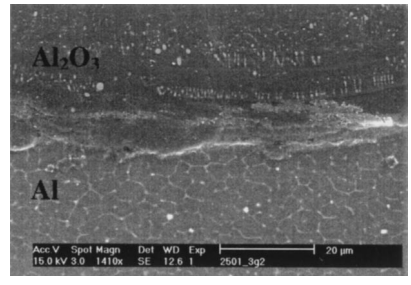

Figure 5. SEM micrograph of a cross-section showing the Al/Al_2O_3 interface.

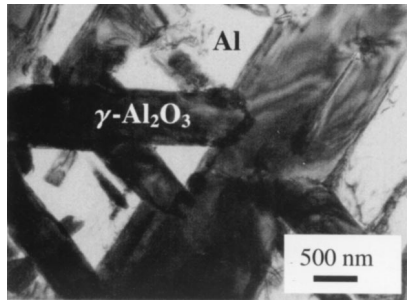

Figure 6. TEM micrograph of the bottom the coating showing the needle-like γ-Al_2O_3 pattern in Al.

than 1200 K, i.e. the maximum temperature at which γ-Al_2O_3 can be formed. Therefore only α-Al_2O_3 is formed, which is rapidly cooled. When the temperature is below 1200 K γ-Al_2O_3 nucleates during cooling till the temperature is below about 800 K. Under the restriction that the cooling rate is high enough to prevent the ordering of atoms that is required to form stable α-Al_2O_3, it means that the lower the cooling rate between 1200 K and 800 K the more γ-Al_2O_3 will be formed.

According to the reasoning described above, it is most likely that γ-Al_2O_3 is located at the top of the coating and near the Al/Al_2O_3 interface. At the top of the coating the Al_2O_3 solidifies later and cools slower than in the middle of the coating. Therefore the temperature is in the γ-Al_2O_3 window for a longer time. At the bottom of the coating liquid Al is present for a longer time since Al is the last phase that solidifies. This time may be used to form more γ-Al_2O_3. γ-Al_2O_3 at the substrate/coating interface is most crucial because this is the place where it is actually needed to improve the bond between the coating and substrate. These predictions are supported by microstructural observations. Figure 5 shows the microstructure of the Al/Al_2O_3 interface. Figure 6 is a TEM micrograph of the bottom region of the coating. A fine needle-like phase, identified as γ-Al_2O_3, is observed.

Conclusions

In the laser treatments performed in this study (scanning speeds between 50 mm/min and 700 mm/min, substrate *uncontrolled*, *cooled* to 15°C or *heated* to 300°C) the cooling rate is high enough (>400°C/s) to form γ-Al_2O_3, for which the ordering requirements are less strict than for α-Al_2O_3. The amount of γ-Al_2O_3 is mainly determined by the actual cooling rate between 1200 K and 800 K, in which γ-Al_2O_3 is formed. The cooling rate should be as low as possible, but still high enough to quench the unstable γ-Al_2O_3. It is likely that γ-Al_2O_3 is formed near the Al_2O_3/Al interface, where it is needed to enhance the bond between coating and substrate.

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